

DFT-Predicted Structural, Vibrational, and Bonding Properties of XSiO and X₂SiO (X = F, Cl, or Br) Molecules

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ABSTRACT: The spectroscopic properties of XSiO (X = F, Cl, or Br) have been predicted using the B3-LYP/6-311 + G(2d) level of theory. It has been shown that the halogen atom is Si bonded in a bent structure, with $\angle(\text{XSiO})$ bond angles close to 126°. The binding energy of the halogen with the SiO subunit was calculated to be -80.1, -40.9, and -29.3 kcal/mol for FSiO, ClSiO, and BrSiO, respectively. The harmonic frequencies and isotopic shifts have been calculated. A comparison between XSiO and X₂SiO has also been made. For the X₂SiO (X = F or Cl) compounds, the calculated frequencies are in fair agreement with the available experimental data. Characterization of bonding has been investigated with different approaches (natural bond orbital approach, topological analysis of the charge density, and of the electron localization function ELF). © 1998 John Wiley & Sons, Inc. J Comput Chem 19: 1205–1214, 1998

Keywords: silicon monoxide halides; IR spectra; DFT; electron localization function; bonding analysis

Introduction

The investigation of lower silicon oxides analogous to known carbon compounds has generated much interest from both experimental^{1–11} and

theoretical^{12–15} points of view. It is well known that small polar inorganic systems built only of electronegative elements are not well described by classical *ab initio* methods.¹⁶ For such compounds, density functional theory (DFT) provides a powerful tool to predict physical and chemical properties at a high accuracy level and with a relatively low computational cost.^{10,11,14,15} Because the preparation of “high temperature” molecules is difficult, the silicon compounds are not yet as well studied as the carbon species, and further theoretical works

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are necessary to reach a better understanding of the different chemistry exhibited by silicon. To our knowledge, there is no experimental study of the XSiO ($\text{X} = \text{F}, \text{Cl}, \text{or Br}$) species, whereas the X_2SiO ($\text{X} = \text{F} \text{ or } \text{Cl}$) ones have been observed in IR spectroscopy experiments.^{8,9}

In this work, the structural and vibrational properties of XSiO and X_2SiO ($\text{X} = \text{F}, \text{Cl}, \text{or Br}$) have been investigated by the DFT approach. In addition, the DFT structural results are compared with those obtained with the Møller–Plesset (MP2) and coupled-cluster [CCSD(T)] methods. Furthermore, to obtain a deeper insight into the bonding of these molecules, a topological analysis of the ELF function¹⁷ has been undertaken. The results are compared with those provided by the natural bond orbital analysis (NBO)¹⁸ and by topological study of the charge density.¹⁹

Computational Details

All calculations have been performed with the Gaussian-94/DFT quantum chemical package.²⁰ The DFT calculations have been carried out with Becke’s three-parameter hybrid method²¹ using the Lee–Yang–Parr correlation functional.²² For open-shell systems, the unrestricted DFT scheme has been retained. The 6-311 + G(2d) basis set of McLean et al.²³ including six Cartesian *d* components has been used for all atoms. For those compounds involving bromine, additional calculations have been carried out with the relativistic pseudopotential of Igel-Mann et al.²⁴ The post-Hartree–Fock calculations have been made at the MP2 and CCSD(T) levels of theory.

We have used the TopMoD package²⁵ developed in our laboratory to perform the topological analysis of the ELF function and the program EXTREME (part of the AIMPAC suite of programs) developed by Bader et al.²⁶

Results and Discussion

STRUCTURAL PROPERTIES

The structural properties and vibrational frequencies of the isolated SiO , X , and X_2 ($\text{X} = \text{F}, \text{Cl}, \text{or Br}$) species are listed in Table I. The calculated parameters are in relatively good agreement with the corresponding available experimental values.²⁷ In the case of Br_2 , the pseudopotential calculation yields a larger internuclear separation (2.447 Å) than both the experimental value and the all-electron calculation. For the sake of homogeneity the 6-311 + G(2d) basis has been used for all molecules investigated here.

The optimized equilibrium parameters of the XSiO and X_2SiO compounds are presented in Table II. To compare the compounds investigated here with their carbonyl counterparts, we studied the CO , ClCO , and Cl_2CO molecules at the same level of theory. Incidentally, the calculated results on the carbonyl compounds²⁸ are in good agreement with the experimental data.²⁹ According to the DFT results, the halogen atoms are bonded on the silicon side in the XSiO and X_2SiO molecules, whereas alkali metals are bonded on the oxygen side of the SiO moiety.^{10,14} The calculation predicts a bent structure for the XSiO and a phosgene-like geometry for the X_2SiO ones, consistent with the XCO^{30} and X_2CO^{31} compounds. The SiO bond distance is always lengthened in

TABLE I. Optimized Equilibrium Parameters for SiO and X_2 ($\text{X} = \text{F}, \text{Cl}, \text{or Br}$).^a

Parameters	SiO^b	F_2	Cl_2	Br_2
r (Å)	1.5144 1.510 ^c	1.3988 1.412 ^c	2.0330 1.987 ^c	2.3416 2.2810 ^c
E (a.u.)	−364.781441	−199.580637	−920.421913	−5148.283444
ω (cm ^{−1})	1249 1241.6 ^c	1035.5 916.6 ^c	541.7 559.7 ^c	309.2 325.3 ^c
f_r (mdyn / Å)	9.35	6.0	3.02	2.22

^aCalculated total energies of the halogen atoms are: $E_{\text{F}} = -99.761965$, $E_{\text{Cl}} = -460.168543$, and $E_{\text{Br}} = -2574.104459$ (a.u.).
^bCalculated dipole moment of SiO is 3.23 D vs. 3.1 D experimentally.²⁷
^cExperimental values (see ref. 27).

TABLE II.
Structural Properties of XSiO and X₂SiO (X = F, Cl, or Br) Molecules.^a

Parameters	FSiO	ClSiO	BrSiO	F ₂ SiO	Cl ₂ SiO	Br ₂ SiO
r_{SiO} (Å)	1.5278	1.5272	1.5266	1.5059	1.5112	1.5133
r_{XSi}	1.6008	2.0811	2.2722	1.5747	2.0278	2.2037
r_{XX}				2.4899	3.2907	3.6046
$\angle(\text{XSiO})$ (deg.)	126.5	125.8	126.0	127.7	125.8	125.1
D_e^b (kcal/mol)	-81.1	-40.9	-29.3	-182.1	-80.0	-55.6
μ (D)	2.65	2.81	2.84	2.25	3.11	3.32

^aGround electronic states are $^2A'$ and 1A_1 for XSiO and X₂SiO, respectively.

^bThe calculated total energies are: $E_{\text{FSiO}} = -464.672675$, $E_{\text{ClSiO}} = -825.015100$, $E_{\text{BrSiO}} = -2938.932627$, $E_{\text{F}_2\text{SiO}} = -564.652199$, $E_{\text{Cl}_2\text{SiO}} = -1285.330796$, and $E_{\text{Br}_2\text{SiO}} = -5513.159644$ a.u. D_e is given by $E_{\text{XSiO}} - E_{\text{X}} - E_{\text{SiO}}$ and $E_{\text{X}_2\text{SiO}} - E_{\text{X}_2} - E_{\text{SiO}}$ for the XSiO and X₂SiO species, respectively.

XSiO with respect to free SiO. It decreases slightly as the atomic number increases (and the electronegativity decreases) when going from FSiO to BrSiO. For the X₂SiO molecules, the SiO bond length is shortened with respect to free SiO, and decreases from F₂SiO to Br₂SiO. The lengthening of the SiO bond distance in XSiO is larger than the shortening of the SiO bond distance in the corresponding X₂SiO. It is worth noting that the CO bond length follows the same trend for CO, ClCO, and Cl₂CO.²⁸ The XSi distance increases with the atomic number in both XSiO and X₂SiO series. This bond length is always larger in the XSiO molecules than in their X₂SiO counterparts. The same trend has been found for ClCO and Cl₂CO.²⁸ The $\angle(\text{XSiO})$ angle varies from 125° to 127° for all compounds investigated here. The dipole moments of both XSiO and X₂SiO increase from X = F to X = Cl, then to X = Br. For XSiO molecules, the dipole moment is smaller than that of free SiO. The same trend holds for the X₂SiO molecules, except for Br₂SiO, the dipole moment of which is slightly larger than that of free SiO. In the case of the carbonyl compounds, the dipole moment increases from free CO to ClCO and then to Cl₂CO (the DFT values are 0.094, 0.43, and 1.24 D for CO, ClCO, and Cl₂CO, respectively). It has been found that the binding energy of the halogen substantially decreases from F to Br for both XSiO (calculated with respect to X and SiO) and X₂SiO (calculated with respect to X₂ and SiO). It is worth noting that the binding energy of the X₂SiO species is nearly twice that of the XSiO counterparts. The same trend has been found for ClCO and Cl₂CO, for which the DFT-calculated values are -11 and -29 kcal/mol, respectively. Table III reports the opti-

mized structural parameters of the F₂, SiO, FSiO, and F₂SiO compounds calculated at the MP2 level of theory, taking into account all electrons, and with the same basis set as in DFT. One can readily verify that the DFT energetic and structural results are very close to those calculated with the MP2 method. Single-point CCSD(T) calculations have been performed at the MP2-optimized geometries for F₂, SiO, FSiO, and F₂SiO molecules. The good agreement between the DFT results and the CCSD(T) results can be intuitively generalized to the compounds containing heavier halogen atoms for which the larger number of electrons (and of basis functions) dramatically increases the CCSD(T) computational cost.

This comparative study gives support to the reliability of the DFT techniques in the study the XSiO and X₂SiO (X = F, Cl, or Br) compounds.

TABLE III.
Structural Properties of F₂, SiO, FSiO, and F₂SiO Molecules from the MP2 Method.^a

Parameters	F ₂	SiO	FSiO	F ₂ SiO
r_{SiO} (Å)		1.5299	1.5278	1.5145
r_{XSi}			1.5940	1.5718
r_{XX}	1.4070			2.4859
$\angle(\text{XSiO})$ (deg.)			128.9	127.7
D_e^b (kcal/mol)			-83.2	-192.3
D_e^c			-73.4	-192.3

^aWith the 6-311 + G(2d) basis set.

^bCalculated electronic energies are: $E_{\text{F}} = -99.605101$, $E_{\text{F}_2} = -199.268347$, $E_{\text{SiO}} = -364.302184$, $E_{\text{FSiO}} = -464.039828$, and $E_{\text{F}_2\text{SiO}} = -563.570531$ a.u.

^cBinding energy calculated from single-point calculations using CCSD(T) at the MP2-optimized geometry.

TABLE IV.
Harmonic Vibrational Frequencies^a in cm⁻¹ (Intensities in Parentheses in km / mol), Isotopic Shifts, and Force Constants for Lowest ²A' State (C_s Symmetry) of XSiO.

Parameters	FSiO	ClSiO	BrSiO
ν_1 (SiO stretch)	1174(77)	1163(64)	1166(64)
$\Delta(^{16}\text{O} / ^{18}\text{O})$	36.2	41.1	41.7
$\Delta(^{28}\text{Si} / ^{29}\text{Si})$	8.6	7.5	7.5
ν_2 (XSi stretch)	810(95)	483(105)	368(78)
$\Delta(^{16}\text{O} / ^{18}\text{O})$	6.2	1.6	1.5
$\Delta(^{28}\text{Si} / ^{29}\text{Si})$	4.0	4.2	4.5
ν_3 (XSiO bend)	291(30)	224(17)	190(9)
$\Delta(^{16}\text{O} / ^{18}\text{O})$	5.9	6.3	6.4
$\Delta(^{28}\text{Si} / ^{29}\text{Si})$	1.7	1.1	0.8
f_{11}, f_{22}, f_{33}	7.95, 3.17, 0.60	8.10, 2.22, 0.51	8.18, 1.64, 0.50
f_{12}, f_{13}, f_{23}	0.107, 0.233, 0.038	0.145, 0.189, -0.008	0.152, 0.164, -0.021

^aAll three vibrational modes are of A' symmetry.

VIBRATIONAL ANALYSIS

Calculated vibrational analysis has been performed at the harmonic approximation. Table IV contains harmonic vibrational frequency data for the XSiO molecules. All isotopic shifts presented in Table IV are red shifts. There are no experimental values for these systems. It should be noted that the SiO frequency in XSiO is significantly red shifted with respect to that of free SiO; that is, 75, 86, and 83 cm⁻¹ for FSiO, ClSiO, and BrClO, respectively. The calculated infrared intensities of the ν_1 and ν_2 modes are strong enough to be

observed experimentally. Moreover, the isotopic shifts are relatively large for all modes. The quadratic force constants of the XSiO molecule presented in Table IV, may be useful for the analysis of future experiments. For the XSiO molecule, the following simple internal coordinates have been used: $S_1 = r_{\text{SiO}}$, $S_2 = r_{\text{XSi}}$, and $S_3 = \angle(\text{XSiO})$.

The calculated and available experimental vibrational frequencies of the main isotopic X₂SiO species, as well as some force constants, are reported in Table V. In 1980, Schnöckel observed the six vibrational modes of X₂SiO (X = F or Cl) by

TABLE V.
Harmonic Vibrational Frequencies in cm⁻¹ (Intensities in Parentheses in km / mol) and Some Force Constants for Lowest ¹A₁ State (C_{2v} Symmetry) of X₂SiO.

Symm.	Type	F ₂ SiO	Cl ₂ SiO	Br ₂ SiO
$A_1\nu_1$	SiO str.	1316(162)	1258(122)	1245(110)
	exp. ^a	1309.4	1239.9	
	f_{11}	9.49	9.25	9.14
ν_2	XSi symm. str.	809(33)	480(21)	341(9)
	Exp. ^a	835.1	501.1	
	f_{22}	5.87	3.03	2.35
ν_3	XSiX symm. bend	343(20)	197(2)	123(0.1)
	Exp. ^a	≈ 423	≈ 200	
$B_1\nu_4$	Wagging	357(86)	287(37)	256(27)
	Exp. ^a	344.3	279.9	
$B_2\nu_5$	XSi asymm. str.	968(199)	613(247)	499(231)
	Exp. ^a	996.0	637.5	
ν_6	Rocking	330(47)	263(32)	223(4)
	Exp. ^a	332.6	269.0	

^aRefs. 8 and 9.

infrared spectroscopy.^{8,9} He assigned the ν_4 , ν_5 , and ν_6 modes to the σ_v plane of C_{2v} symmetry. In the present work (Table V), where Wilson's convention is adopted, the assignment of the ν_4 , ν_5 , and ν_6 modes are made with respect to the σ_v plane of C_{2v} symmetry. An inspection of the IR spectra indicates that all the IR intensities compare well with the experimental data. The calculated and observed isotopic shifts are also in good agreement, as shown in Table VI. Except for the ν_3 mode of F_2SiO (FSiF symmetric bending), the calculated frequencies are in good agreement with the experimental values. One can readily note that for Cl_2SiO the predicted experimental value of the ν_3 mode is very close to the calculated value. On the other hand, the relatively large calculated $^{16}O/^{18}O$ isotopic shift of the ν_3 mode of F_2SiO (1.9 cm^{-1}) should enable the observation of the isotopic band. It should be noted that the SiO frequency is blue shifted in the F_2SiO and Cl_2SiO molecules, whereas it is slightly red shifted in the Br_2SiO compound. The absolute value of this frequency shift significantly decreases from F_2SiO to Cl_2SiO and then to Br_2SiO (the DFT shifts are -67.3 , -9.4 , and 4.1 cm^{-1} for F_2SiO , Cl_2SiO , and Br_2SiO , respectively). However, the SiO force constant variation is consistent with the frequency

shift. It is important to note that the CO frequency is much more red shifted in both $ClCO$ and Cl_2CO with respect to the free CO molecule (of 258 and 338 cm^{-1}),²⁷ than the SiO frequency in $ClSiO$ (of 85.9 cm^{-1}). In Cl_2SiO , this latter frequency is weakly blue shifted by -9.4 cm^{-1} .

BONDING CONSIDERATIONS

Mulliken, NBO, and Laplacian of Charge Density Analyses

Table VII lists the calculated atomic charges and the topological properties at the bond critical points. The atomic charge populations in the $XSiO$ and X_2SiO compounds obviously indicate a relatively large charge transfer from the SiO subunit to the halogen atom. This charge transfer occurs essentially from the Si atom to the halogen atom. It should be noted that for both $XSiO$ and X_2SiO compounds the atomic charge borne on the halogen atom follows the same trend as the binding energy. According to the topological theory of atoms in molecules¹⁹ the positive values of the electron density Laplacian at the bond critical point (bcp, where $\nabla\rho = 0$) are associated with closed-shell interactions (ionic bonds, hydrogen bonds,

TABLE VI.
Isotopic Frequency Shifts in cm^{-1} for Lowest 1A_1 State of X_2SiO .

Parameters	Type	F_2SiO	Cl_2SiO	Br_2SiO
$A_1\nu_1$	SiO str.			
$\Delta(^{16}O/^{18}O)$	DFT (exp. ^a)	36 (31.4 ± 0.2)	42 (36.7 ± 0.3)	43
$\Delta(^{28}Si/^{29}Si)$	DFT (exp. ^a)	10.8 (10.4 ± 0.2)	9.2 (9.4 ± 0.2)	8.4
ν_2	XSi symm. str.			
$\Delta(^{16}O/^{18}O)$	DFT (exp. ^a)	11.3 (12.1 ± 0.1)	5.2 (5.7 ± 0.3)	5.1
$\Delta(^{28}Si/^{29}Si)$	DFT (exp. ^a)	0.8 (0.6 ± 0.3)	1.4	2.1
ν_3	XSiX symm. bend			
$\Delta(^{16}O/^{18}O)^b$	DFT	1.9	1.1	0.6
$\Delta(^{28}Si/^{29}Si)^b$	DFT	0.8	0.5	0.6
$B_1\nu_4$	Wagging			
$\Delta(^{16}O/^{18}O)$	DFT (exp. ^a)	3.5 (3.6 ± 0.3)	3.7 (3.3 ± 0.3)	3.8
$\Delta(^{28}Si/^{29}Si)$	DFT (exp. ^a)	4.1 (3.8 ± 0.3)	3.5	3.1
$B_2\nu_5$	XSi asymm. str.			
$\Delta(^{16}O/^{18}O)$	DFT (exp. ^a)	0.0 (< 0.2)	0.24 (0.2)	0.6
$\Delta(^{28}Si/^{29}Si)$	DFT (exp. ^a)	8.0 (8.1 ± 0.4)	7.9 (7.2 ± 0.3)	7.2
ν_6	Rocking			
$\Delta(^{16}O/^{18}O)$	DFT (exp. ^a)	8.6 (8.5 ± 0.5)	9.5 (9.8 ± 0.3)	9.7
$\Delta(^{28}Si/^{29}Si)$	DFT (exp. ^a)	1.0 (0.9 ± 0.3)	0.3	0.0

^aRefs. 8 and 9.

^bThere is no experimental value.

TABLE VII.
Topological Properties of Species Studies.^a

Compounds	q_x	q_{Si}	q_O	$\rho(r_c)$	$\nabla^2\rho(r_c)$	$H(r_c)$	r_c
SiO		1.376	-1.376	0.195	1.461	-0.104	Si—O
FSiO	-0.823	2.121	-1.298	0.187	1.281	-0.101	Si—O
				0.139	0.947	-0.046	F—Si
ClSiO	-0.640	1.943	-1.302	0.186	1.304	-0.101	Si—O
				0.095	0.086	-0.058	Cl—Si
BrSiO	-0.500	1.801	-1.304	0.187	1.315	-0.100	Si—O
				0.082	-0.041	-0.048	Br—Si
F ₂ SiO	-0.809	3.032	-1.413	0.199	1.408	-0.155	Si—O
				0.151	1.067	-0.054	F—Si
Cl ₂ SiO	-0.675	2.748	-1.398	0.196	1.393	-0.111	Si—O
				0.106	0.137	-0.068	Cl—Si
Br ₂ SiO	-0.563	2.509	-1.384	0.195	1.383	-0.110	Si—O
				0.093	-0.013	-0.060	Br—Si

^aElectron density ρ in $e/\text{\AA}^3$, Laplacian ∇^2 in $e/\text{\AA}^5$, and energy density H in hartree/ \AA^3 at the bond critical point r_c .

and van der Waals molecules), whereas $\nabla^2\rho < 0$ indicates shared interactions (covalent bonds). The results reported in Table VII show that, following this criterion, the SiO bond should be considered as a closed-shell interaction for all compounds, because of the positive Laplacian. Another criterion, proposed by Cremer, states that the local energy density, $H(r_c)$, at the bond critical point, should be positive for ionic bonds and negative for partly covalent bonds.³² The values of $H(r_c)$ displayed in Table VII lead to a conclusion that contradicts the analysis of the Laplacian. However, an indication of the ionic character of the SiO bond and of its evolution throughout the series is provided by the oxygen atomic charge. Figure 1 displays the oxygen charge calculated from the Mulliken population analysis, the NBO analysis, and from the topological analysis of the charge density, versus the SiO bond length. It is worth noting that the Mulliken analysis underestimates the bond ionicity with respect to both NBO and Bader analyses. Moreover NBO yields values intermediate between those obtained by the two other methods. The evolution of the oxygen charge with respect to the SiO distance exhibits a clear correlation for the topological approach, whereas, for the NBO and Mulliken analyses, the results are more scattered and therefore do not allow reliable conclusions. For a mostly ionic bond, one could expect from electrostatics that an increase of the absolute oxygen charge would shorten the bond distance, which is clearly observed for the topological atomic charges. On the contrary, the opposite trend is

expected for a dominant covalent character which can only be verified for the FSiO/F₂SiO pair.

Topological Analysis of ELF Function

The topological analysis of the ELF function provides an alternative partition scheme of the molecular space into basins of attractors that have a clear chemical signification. These basins are

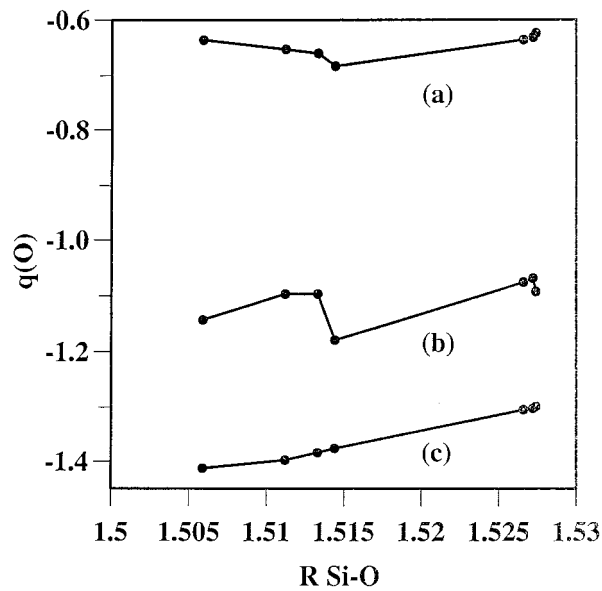


FIGURE 1. Oxygen charge variation versus the Si—O distance. Oxygen charge calculated from (a) Mulliken analysis, (b) NBO method, and (c) topology of electron density.

either core basins surrounding nuclei or valence basins. The valence basins are characterized by their synaptic order, which is the number of core basins with which they share a common boundary. Accordingly, monosynaptic basins correspond to lone-pair regions, whereas di- and polysynaptic basins correspond to bonding regions. The basins are labeled $T_{[i]}$ (atom labels). T denotes the type of basin, V is valence and C is core; i is an optional running number in the case of multiple basins related to the same atom(s). For example, in the water molecule there is one core basin for the oxygen K -shell labeled $C(O)$, two protonated disynaptic basins, $V(H_1, O)$ and $V(H_2, O)$, and two monosynaptic basins corresponding to the lone pairs $V_1(O)$ and $V_2(O)$. The partition into basins allows the calculation of related properties by integration of the property densities over the basins.^{33,34} In particular, for a basin labeled Ω_A , one can define the average population as:

$$\bar{N}(\Omega_A) = \int_{\Omega_A} \rho(\mathbf{r}) d\mathbf{r} \quad (1)$$

The integrated spin density, $S_z(\Omega_A)$, is:

$$\bar{S}_z(\Omega_A) = \frac{1}{2} \int (\rho^\alpha(\mathbf{r}) - \rho^\beta(\mathbf{r})) d\mathbf{r} \quad (2)$$

A measure of the delocalization is provided by the variance of $\bar{N}(\Omega_A)$:

$$\begin{aligned} \sigma^2(\bar{N}; \Omega_A) &= \langle N^2 \rangle_{\Omega_A} - \langle N \rangle_{\Omega_A}^2 \\ &= \bar{N}(\Omega_A, \Omega_A) - \bar{N}(\Omega_A)(\bar{N}(\Omega_A) - 1) \end{aligned} \quad (3)$$

in which $\bar{N}(\Omega_A, \Omega_A)$ is the actual number of electron pairs within Ω_A ; that is, the integral over Ω_A of the pair function $P_2(\mathbf{r}_1, \mathbf{r}_2)$:

$$\bar{N}(\Omega_A, \Omega_A) = \int_{\Omega_A} d\mathbf{r}_1 \int_{\Omega_A} d\mathbf{r}_2 P_2(\mathbf{r}_1, \mathbf{r}_2) \quad (4)$$

Formally, the variance is the difference between the actual number of electron pairs, $\bar{N}(\Omega_A, \Omega_A)$, and the expected number of pairs for a noninteracting basin of population $\bar{N}(\Omega_A)$. It has been shown³⁵ that eq. (3) can be transformed into:

$$\begin{aligned} \sigma^2(\bar{N}; \Omega_A) &= \sum_{B \neq A} \bar{N}(\Omega_A) \bar{N}(\Omega_B) - \bar{N}(\Omega_A, \Omega_B) \\ &= \sum_{B \neq A} B(\Omega_A, \Omega_B) \end{aligned} \quad (5)$$

allowing for the analysis of the variance of the population of a given basin, Ω_A , in terms of contributions arising from the other basins. An alternative expression of the $B(\Omega_A, \Omega_B)$ contributions can be obtained by writing the pair function as:

$$P_2(\mathbf{r}_1, \mathbf{r}_2) = \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) [1 + h(\mathbf{r}_1, \mathbf{r}_2)] \quad (6)$$

in which $h(\mathbf{r}_1, \mathbf{r}_2)$ denotes the exchange correlation hole,³⁵ hence:

$$B(\Omega_A, \Omega_B) = - \int_{\Omega_A} d\mathbf{r}_1 \int_{\Omega_B} d\mathbf{r}_2 \rho(\mathbf{r}_1) \rho(\mathbf{r}_2) h(\mathbf{r}_1, \mathbf{r}_2) \quad (7)$$

When the wave function is expressed by a single determinant:

$$\begin{aligned} B(\Omega_A, \Omega_B) &= \sum_i \sum_j (n_i^\alpha n_j^\alpha + n_i^\beta n_j^\beta) \langle \phi_i | \phi_j \rangle_{\Omega_A} \langle \phi_j | \phi_i \rangle_{\Omega_B} \end{aligned} \quad (8)$$

in which $\langle \phi_i | \phi_j \rangle_{\Omega_A}$ is the partial overlap of the ϕ_i and ϕ_j orbitals. Therefore, the matrix elements, $B(\Omega_A, \Omega_B)$, provide an indication of the basins involved in the delocalization. The larger the $B(\Omega_A, \Omega_B)$, the larger the delocalization between Ω_A and Ω_B . It is worth noting that, in the case of atomic basins in the sense of Bader, the $B(\Omega_A, \Omega_B)$ values are identical to the half topological bond orders defined by Ángyán et al.³⁷ from a different starting point. These latter bond orders are invariant with respect to unitary transformations of the orbitals in contrast to the findings of Cioslowski and Mixon.³⁸ In the case of the *ELF* function basins, the $B(\Omega_A, \Omega_B)$ values no longer have the signification of bond orders, but rather that of delocalization orders.

Figure 2 displays the 0.8 and 0.75 localization domains³⁹ of the X_2SiO and $XSiO$ species, respectively. For both X_2SiO and $FSiO$ molecules there are no $V(Si, O)$ disynaptic basins, whereas $V(Si, X)$ is always present. This is a strong argument to consider the SiO bond as ionic in both compounds. Moreover, in the case of $BrSiO$ and Br_2SiO , the $V(Si, Br)$ localization domains are well-separated from the $V(Br)$ domains, which correspond to the Br lone pairs. The valence basin populations are reported in Table VIII. The $Si-X$ bonds are characterized by a disynaptic basin in all systems. The $V(Si, X)$ population increases from $XSiO$ to X_2SiO , and within each stoichiometry it decreases as the electronegativity of the halogen increases. The

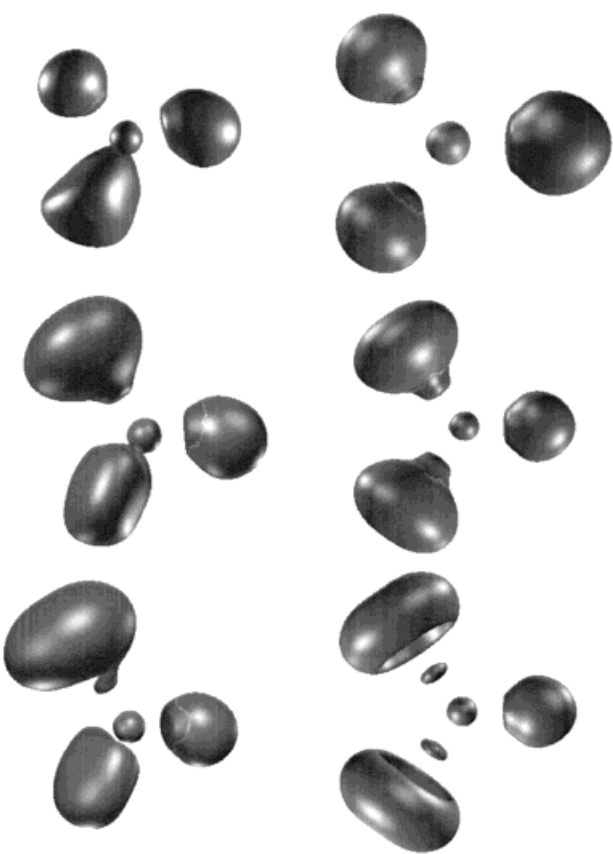


FIGURE 2. Localization domains of the X_2SiO (left $ELF = 0.8$ bounding isosurfaces) and $XSiO$ (right $ELF = 0.75$ bounding isosurfaces) species. From top to bottom, $X = Br, Cl, F$. The nature of the attractor(s) defining the domain is given by the color code. Magenta: core; green: valence disynaptic; blue: protonated valence disynaptic. This figure, presented here in black and white, is available in color at <http://journals.wiley.com/jcc/>

standard deviation of $V(Si, X)$ is of the order of $1 e^-$, and delocalization occurs mainly with the lone-pair basin; that is, $V(X)$. Due to the delocalization of the (Si, X) basin, the halogen lone-pair populations are larger than $6 e^-$, indicating a partial ionic character of the bond. For the X_2SiO and

$FSiO$ species, there is no disynaptic basin between Si and O . The oxygen atom appears to be mostly ionic, because its lone-pair population exceeds $7 e^-$. In the remaining cases of $ClSiO$ and $BrSiO$, the disynaptic basin $V(Si, O)$ exists and has a population close to $2 e^-$ as expected for a single bond. In

TABLE VIII.
Topological ELF Population Analysis (in e^-).

Compounds	$V(Si)$	$V(Si, O)$	$V(Si, X)$	$V(O)$	$V(X)$
SiO	2.38 (0.88)	3.18 (1.21)		4.22 (1.20)	
$FSiO$	1.44 (0.84)		0.90 (0.82)	7.39 (1.00)	6.81 (1.06)
$ClSiO$	1.53 (0.89)	2.01 (1.09)	1.02 (0.86)	5.35 (1.22)	6.74 (1.14)
$BrSiO$	1.51 (0.89)	1.97 (1.09)	1.18 (0.92)	5.39 (1.22)	6.87 (1.37)
F_2SiO			1.05 (0.87)	7.81 (0.90)	6.73 (1.07)
Cl_2SiO			1.44 (0.97)	7.76 (0.97)	6.46 (1.15)
Br_2SiO			1.60 (1.02)	7.70 (0.99)	6.62 (1.37)

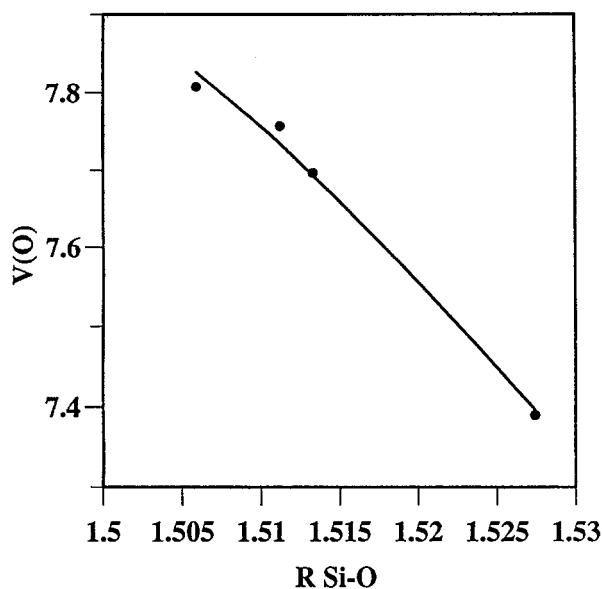


FIGURE 3. The oxygen lone-pair population of different compounds, obtained from the topological analysis of the ELF function, versus the Si—O distance.

the SiO molecule, the (Si, O) basin population is intermediate between a single and a double bond. The large standard deviation indicates a delocalization between the Si—O bond and the oxygen and silicon lone pairs. For ClSiO and BrSiO, $V(O)$ basin populations are close to $5.35 e^-$ and, therefore, the Si—O bond is partly ionic. As depicted in Figure 3, the oxygen lone-pair population is correlated with the Si—O distance, which increases as the population decreases. This result is in agreement with the correlation obtained with the oxygen atomic populations (Fig. 1) and is consistent with the electrostatic interpretation given earlier. The integrated spin density of the silicon lone-pair basin $V(Si)$ is calculated to be 0.29, 0.27, and 0.26 for FSiO, ClSiO, and BrSiO, respectively. It is always very small for the $V(Si, X)$ basins (< 0.02). The remaining spin density is distributed on the oxygen and halogen lone pairs.

Conclusions

The geometries, binding energies, and vibrational frequencies of the $XSiO$ ($X = F, Cl, \text{ or } Br$) molecules have been predicted using the DFT method. The X_2SiO ($X = F, Cl, \text{ or } Br$) molecules have also been investigated at the same level of theory. It has been shown that the binding energy decreases in going from FSiO to ClSiO and then to

BrSiO. The same trend holds for the X_2SiO compounds. The SiO stretching mode of the $XSiO$ molecules is largely red shifted with respect to free SiO. In the case of X_2SiO , the calculated frequencies are in good agreement with experimental data. The SiO stretching mode is blue shifted in the F_2SiO and Cl_2SiO molecules compared with the free SiO molecule, whereas it is slightly red shifted for the Br_2SiO molecule. The atomic charge and the nature of the chemical bonding in all molecules investigated have been studied using topological analyses of the ELF function. It has been shown that there is a single bond between Si and O only for ClSiO and BrSiO, whereas the oxygen atom appears to be mostly ionic for the other molecules. The bonding between the halogen and silicon atoms is characterized by the presence of a disynaptic basin. Moreover, topological analysis of the ELF function has clearly pointed out that the oxygen lone-pair population is correlated with the Si—O bond length. The same trend holds between the oxygen atomic charge obtained from the topology of the electron density and the Si—O distance. Finally, we hope that these theoretical predictions will be helpful in the search for $XSiO$ molecules by experimental techniques.

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